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"Laser Initiated Ignition of Liquid Propellant"

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FINAL TECHNICAL REPORT

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INTRODUCTION

All the objectives proposed for this research have broadly been met. The first part of the work was summarised in a paper entitled "Laser Ignition of Liquid Propellants" which was presented at the 23rd International Combustion Symposium in Orleans, France, and will be published in the symposium proceedings in due course. A modified text is enclosed as an Appendix by way of summarising first stage results and reviewing the experimental techniques developed for this research. During the last six months, all the remaining avenues of study have been pursued to their conclusions:

Using various propellants and varying initiating energies, heating (followed by periods at room temperature), and dyeing to vary absorption, were investigated in various combinations with electrolysis, to assess whether or not the effects were additive. Addition of methylene blue was compared with black pigment in order to assess any contribution of the nitrate contained in the former. Supplementary work was done on focusing outside the droplet, in order to study the effect of the constitution of the gaseous plasma on the process. Thus, focusing in helium was compared with results for air and the study was then extended to deliberately adding nitrogen oxides by focusing in the vicinity of solid potassium nitrate crystals. The results and conclusions are summarised below.

RESULTS

Effects of Precursory Electrolysis, Heat Treatment and Dyeing

It had previously been reported (7th Interim Report) that propellant decomposition is essentially unaffected by the duration of the "rest period" between electrolysis and laser pulse, whether focusing is within (Figs. 1 and 2) or outside (Fig. 3) the propellant droplet and even when the laser pulse is delayed until next day. These figures indicate also the level of scatter.
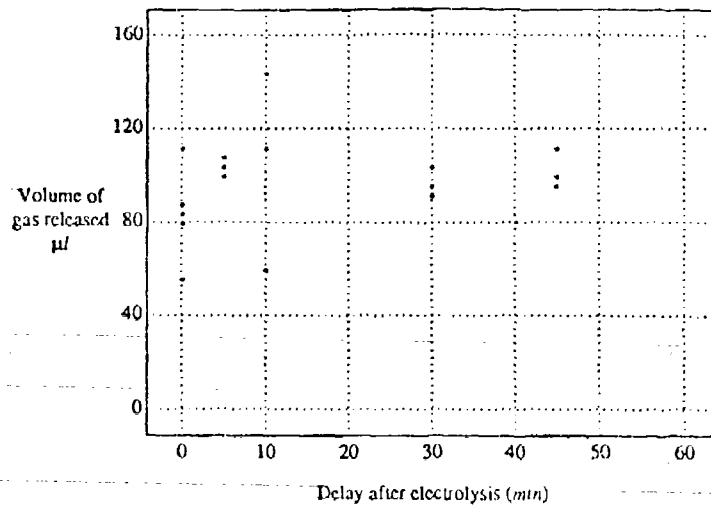
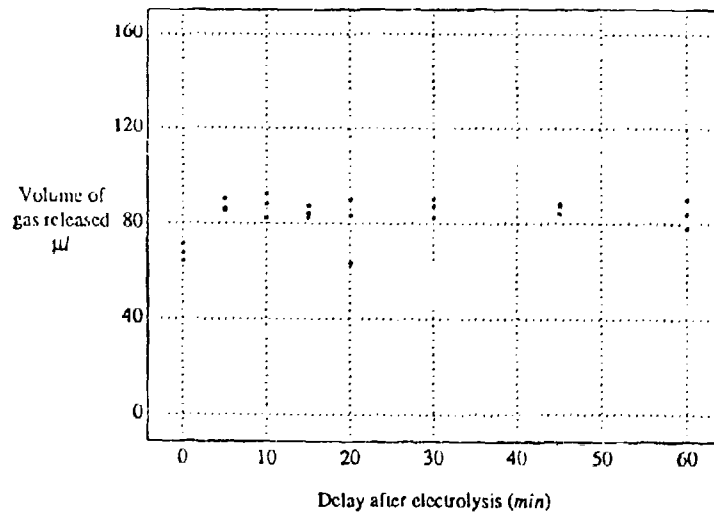Fig 1 - Effect of delay after electrolysis on LP-101

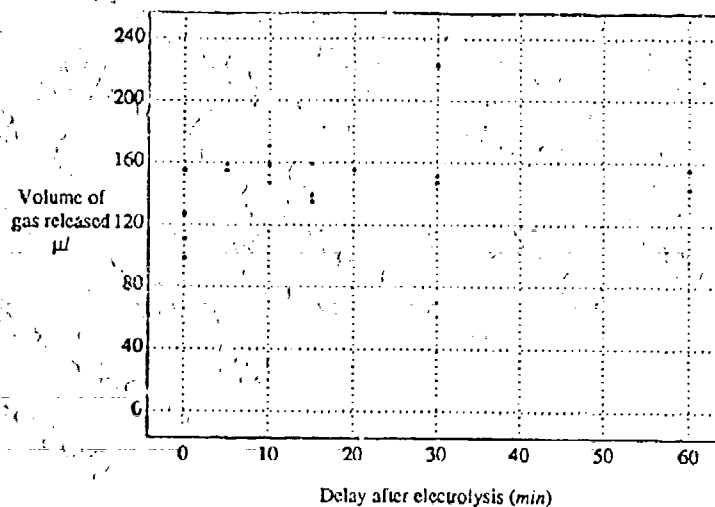Fig. 2 - Effect of delay after electrolysis on HAN/SBAN

Fig. 3 - Effect of delay after electrolysis on HAN/SBAN

We conclude that the propellant is permanently altered by precursory electrolysis and that focusing outside the drop produces more decomposition. This is attributed to the combined effects of the plasma and shock wave generated during breakdown. It will be shown below that the NO formed in the air plasma also plays a part. As previously reported, there is little or no difference between the results for Q-switched and free running pulses at the same total energy.

Heat treatment followed by varying rest periods has much the same effect as electrolysis. Three propellant mixtures were used for this test: LP-101, HAN/SBAN and HAN/DEAN The study involved heating many small (50µl) samples of propellant individually in small glass containers held in a water bath of constant temperature 70°C. A larger vessel containing approximately 2ml of propellant was also heated in each experiment and the sample was used for laser initiation measurements later. The temperature was held constant by an electrical heater switched by a temperature controller. A stirrer and forced water circulation ensured that all samples were kept at the same temperature. The water was first heated to the final

temperature and then the sample cylinders were immersed in it and kept in place for 7 hours.

Figs. 4-7 show the effect as a function of beam energy, given here in terms of capacitor voltage. Over the relevant range, the measured energy (J) is accurately equal to

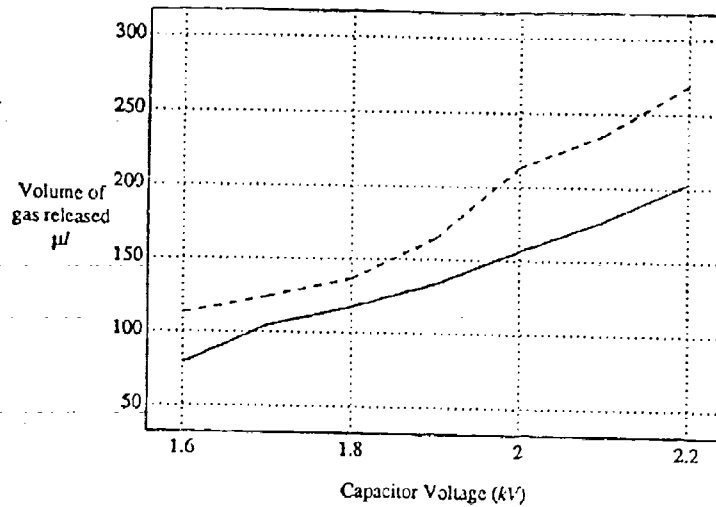$2.98 - 15.13V + 9.31V^2$, where V is the capacitor voltage (kV).

Fig. 4 - Effect of electrolysis on LP-101 - variation with beam energy. The upper curve is for electrolysed samples.
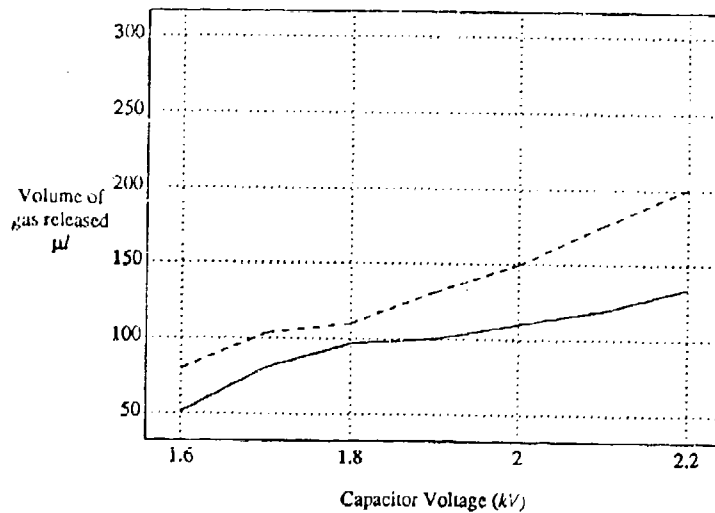

Fig. 5 - Effect of electrolysis on HAN/SBAN - variation with beam energy. The upper curve is for electrolysed samples.
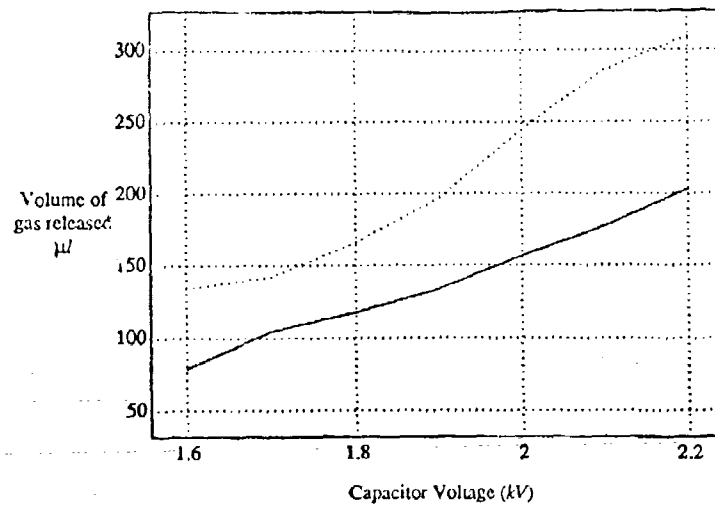
Fig. 6 - Effect of heating on LP-101 - variation with beam energy. The upper curve is for
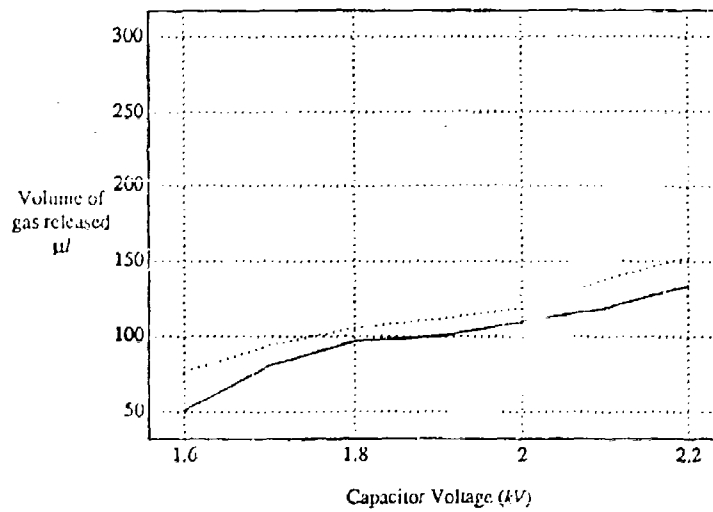
heated samples.

Fig 7 - Effect of heating on HAN/SBAN - - variation with beam energy. The upper curve is

for heated samples.

The effect of heating tends to be less reproducible, as might be expected for a form of preactivation that depends on temperature through an Arrhenius factor. In the case of LP-101 the effect is quite large and, in one isolated case, a sample decomposed spontaneously after three hours. This may point to a potential hazard in applying precursory heat treatment (intentionally or accidentally) to military propellants.

Having established the variation with beam energy, the remaining measurements were carried out at a constant beam energy of 8 joules, near the middle of our experimental range.

The interaction between the laser pulse and the liquid is not well understood. Unlike in the case of breakdown in a gas, it is not obvious that a plasma must be formed initially but, since the propellants are all transparent liquids, heating is not an obvious mechanism either. To investigate this matter further, we focused the laser beam on propellant samples dyed so that they would absorb in the visible and, more specifically, in the red part of the electromagnetic spectrum. Propellant samples were dyed with methylene blue but, since this is a nitrate salt which may have a chemical effect also, comparative experiments were carried out with traces of black drawing ink and also black water colour. The aim of the comparison was to produce a suspension of small black absorbent particles without any chemical modifications.

The maximum increase in decomposition with dyed droplets was about 30%. This applied for methylene blue and drawing ink for free running laser pulses. In the comparison with black water colour carried out with a Q-switched beam, however, the increase in decomposition due to the water colour was less than 10% - barely above the shot-to-shot variation.

In the absence of a full analysis of the ink and water colour dyes, this matter cannot be conclusively resolved. However, we can infer the mechanism from the above observations. If this involved heating of the liquid and the dye made all the difference in absorbing the beam energy, we would expect all absorbers to perform equally well, independent of the switching mode, and also the effect to be much greater than 30% - see the lower curves in Figs 4-7. The difference due to Q-switching would be expected if the droplet was first shattered and then a plasma formed. Q-switching would curtail the time available for this process, unless multiple

spiking occurred. A 30% increase due to the nitrate content of a trace of methylene blue seems reasonable in terms of our electrolytic results.

Effect of Plasma Constitution - Focusing Outside the Droplet

We reverted to measuring the interaction between the laser generated plasma and the droplet not only because the amount of decomposition exceeded that for focusing within the droplet but mainly because of the opportunity of varying the plasma constitution. Numerical values were obtained by averaging four successive measurements, all at a constant beam energy of 8 Joules.

Somewhat to our surprise, there was no appreciable difference (less than 2%) as between Q-switched and free running pulses. The standard deviation, however, was more than double for Q-switching - typically 7% of the average as compared with 3% in the case of free running.

Taking the volume displacement of approx. 200 μl for HAN/SBAN as standard, precursory electrolysis would increase this to 259 μl - i.e. typically by 30%. Dyeing the droplet with methylene blue had no effect. No effect would, of course, be expected due to any changes in transparency of the liquid since the focus was external to it; however, the result indicates that the addition of nitrate involved does not affect the result, at least for interaction with an external plasma.

Replacing the surrounding air by helium, however, significantly decreased the displacement due to decomposition - from 200 to 100 μl. This is all the more remarkable if we bear in mind that, for a given laser beam energy, the temperature of the helium plasma would be expected greatly to exceed that of an air plasma. We conclude that nitric oxide produced in an air plasma must substantially promote the propellant decomposition.

These results encouraged us to increase the NO content of the plasma artificially by exposing a thin platinum wire coated with potassium nitrate to the focused laser pulse. Focusing near metallic objects promotes breakdown because the strong electromagnetic field near the focus is able to extract electrons from the surface. A blank experiment with a platinum wire 1-1.5mm ahead of the droplet indeed produced a small increase in decomposition - by 4 -

5%. When the same 5μm wire was moistened and dipped into powdery potassium nitrate prior to the discharge, decomposition increased by some 43%. Once again, this is all the more extraordinary in view of the considerable cooling of the plasma which must have occurred due to vaporisation of the potassium nitrate and associated water. We conclude that increasing the nitric oxide content of the plasma has a strongly promoting effect on decomposition in the case of initiation by an external plasma.

Cumulative Effects

The object of this part of the study was to ascertain whether, having produced the maximum improvement possible by precursory electrolysis, for example, any further improvement would result from heat treatment, dyeing with methylene blue, etc., both for focusing externally and internally to the droplet. The number of possible permutations and combinations, taking these perturbations singly, in pairs, and so forth, is so large that we shall save much space by reporting only our conclusions rather than listing the extensive aggregate of individual findings.

The outcome was, simply, that the various perturbations are not additive or interactive. Broadly speaking, pre-electrolysis and heat treatment each increases decomposition by some 50%, whilst dyeing with methylene blue or drawing ink results in approx. 30% increase. When these are combined in various ways the resulting improvement is always equal to the largest improvement due to a single governing parameter. The system behaves as if a maximum effect can be produced by a certain amount of NO - if that is the causative agency - and once this amount is reached, by whatever method, no further promotion is achievable. From the practical point of view, this allows us to choose between different methods of promotion on the ground of practical convenience alone.

CONCLUSIONS

An extensive series of quite complex experiments have led to what is essentially a very simple conclusion: that NO and possibly other oxides of nitrogen strongly pre-sensitise the decomposition of every liquid propellant tested. The NO may be produced by precursory

electrolysis, by subjecting the propellant to heat treatment, by adding a nitrate containing compound to it, and even by producing NO externally in a laser plasma focused onto a nitrate crystal. These effects are not cumulative i.e. they increase with increasing NO production only until a certain maximum has been produced, by whatever means.

The proportion of propellant decomposed, however, is not subject to such a ceiling, even though all the measurements were carried out at atmospheric pressure (we would, of course, expect much more complete decomposition had we allowed pressure rise by confinement). It increases with the amount of laser energy deposited and varies for different forms of initiation. Much more decomposition is produc d by a laser focused outside rather than within the droplet (so much so that in the preliminary work, non-military propellants were treated, on visual evidence, as not reacting chemically at all in the latter case - see Appendix), presumably because of the higher temperature and the shock wave generated. This method also lends itself tc studying the effects of plasma - generated species on the propellant reaction.

From the practical point of view, the method of pre-activation can therefore be chosen on the basis of what is most convenient and feasible. From that point of view, electrolysis is outstandingly the most attractive, since it does not require the bulk of the propellant to be permanently pre-treated (as addition of nitrate would) and is much more controllable and less destabilising than heating. It could be carried out on the smallest of scales, e.g.in a duct of the flow system just ahead of the point of use of the propellant.

APPENDIX

Abstract

Following previous studies of electrical ignition of liquid propellants in plasma jets, initiation by focused laser beams is studied both by fast cine shadowgraphy and by recording permanent gas release as a measure of decomposition. Unlike military propellants, droplets of aqueous mixtures of nitrate salts of hydroxylamine with a 4-carbon aliphatic amine do not ignite when an approx 10 J laser pulse is focused within the liquid. Ignition is achieved by producing breakdown in air in the vicinity of propellant droplets, though little decomposition results, at atmospheric pressure. Precursory electrolysis of varying duration is attempted, in view of postulated chemical mechanisms which suggest that solution of N_2O in the propellant should enhance ignition. This indeed greatly promotes the vigour of the reaction and leads to an amount of decomposition which increases with increasing time of electrolysis. It appears that the propellant is permanently modified by this simple procedure, leading to obvious practical as well as fundamental conclusions.

1. Introduction

Previous publications (1-3) have described studies of pulsed plasma jets fed with liquid propellant as high energy ignition plugs. The propellants used in the majority of the experiments consisted of aqueous mixtures of nitrate salts of hydroxylamine and a 4-carbon aliphatic amine which are highly stable and particularly suited to academic research. Some comparative experiments using a military propellant - LP 101 (U.S. LGP 1845) - were also carried out. Ultra high speed shadowgraphy applied to optically accessible plug models was used to observe details of electrical energy transfer to the propellant and the subsequent decomposition and ejection processes.

Depending on the electrical variables and on the plug geometry, processes corresponding to a variety of potential applications, ranging from slow ejection of propellant to very violent events

associated with the emission of shock waves, could be generated at will. In particular, two sequential steps (referred to as "event 1" and "event 2") were identified: a precursory electrolytic phase followed by a much more vigorous process associated with a plasma discharge. In addition to monitoring current and voltage transients, streak shadowgraphy enabled us to follow the energy release due to micro-explosions of individual droplets, following their expulsion from the plug. At atmospheric pressures and in the absence of confinement this energy release could be made be to occur by way of a very large number of small explosive events.

The present research is also concerned with fundamentals of propellant ignition and is confined to the study of individual drops at atmospheric pressure. Initiation, however, is primarily by a focused Q-switched laser beam. The ultimate practical objective is to explore an alternative configuration of a plasma ignition plug, in which electrical leads are replaced by an optical light guide, thus eliminating problems associated with radio interference and the risk of mis-fire due to induction by strong electromagnetic fields. On the fundamental side, the method affords the opportunity for studying the effect of precursory electrolysis, separate from electrical initiation and also for releasing relevant species into the laser plasma by coating them on fibres at the focus of the beam so as to allow for the sudden release and onset of specific reactions with the propellant.

2. Experimental

Two initiating lasers were available: a Laser Associates 211A passively Q-switched ruby, capable of delivering in excess 10 J and an "Apollo" 5 J pulsed ruby laser, Q-switched by a Pockell cell. Short focal length (see below) lenses were used for focusing, after a precursory study showed Fresnel lenses to be only 20% efficient in transmitting light. The single propellant droplet was suspended in a loop of thin platinum wire, or between two such loops which could be used as electrodes in studies involving electrolysis or electrical initiation of the reaction. In the latter case, the two loops were connected to the electrical power supply used in our previous studies (e.g.1, 2). Precise control of the position and separation of the electrodes

was achieved by retaining them in a specially designed support, clamping heavier gauge wire which was used as leads to the fine loops. The waist of the focused laser beam was always small by comparison with the droplet diameter. As in our previous work, the volume of individual droplets was confined to about 30 μl.

The high time-resolution optical system set up at right angles to the initiating beam, was essentially similar to that used during the previous work (2, 4, 5). The light source is a 4W c.w. Ar ion laser, operating at 488 nm, whose beam was pulsed at 30.1 kHz by a cavity dumper, spatially filtered and made parallel by a Schlieren mirror. The exploding droplet was located in this beam and near the focal plane of a rotating mirror camera. The test space was imaged on the rotating mirror rather than on the receptor, in order to maintain the illuminated area of the mirror as small as possible. This results in shadow photography in which the outlines are somewhat blurred by a pattern of diffraction fringes. Any luminosity occurring in the test space is diffuse on the record. The event was recorded on Ilford HP5 monochrome film.

Preliminary experiments exploding droplets of propellants. following purely electrically initiation, showed identical dependence on electrical parameters as in our previous work. There is a voltage threshold above which the event becomes very vigorous. When large droplets are used, not all the liquid is decomp.sed and small satellite droplets are seen to be left over. Again as before, the behaviour of propellants in this system was compared with that of aqueous solutions of salt, which have similar electrical properties but are not capable of decomposing chemically.

3. Laser Initiation

A wide ranging series of experiments was carried out to study the interaction between the focused laser beam and propellant droplets supported on single platinum wire loops. (Some previous studies of such interactions have been carried out with inert liquid droplets - e.g. ref. 6. - but not, to our knowledge, with propellants or with a view to ignition.) The variables

studied included the position of the droplet with respect to the focal point, the focal length of the lens, Q-switching or free running of the laser, type of propellant and the transparency of the propellant droplet to laser light which was varied by dyeing the propellant with methylene blue.

Experiments with "long" focal lengths of 5, 10 and 20 cm always led to shattering and dispersion of the droplets, irrespective of whether the beam was Q-switched or not. Although dispersion occurs in all directions, it appears not to be entirely symmetrical, showing a preponderance of spray in the direction of propagation of the laser beam. Glass slides flanking the droplet upbeam and downbeam both became covered with spray, but the distribution was approximately 60:40 in favour of the slide furthest from the laser, suggesting a mechanical effect. The results were highly reproducible but, unlike in the case of the military propellant, there was never any evidence of droplet decomposition with the hydroxyl ammonium nitrate / 4-carbon aliphatic amine propellant compositions.

A Q-switched laser focused by a short (2cm or less) focal length lens will readily produce breakdown in air, as evidenced by a flash of light and a loud crack. The formation of the plasma which then absorbs more laser energy is narrowly confined to the region of large electromagnetic field around the focus. The initial electron supply can be enhanced by arranging for the focal spot to occur close to a metal surface, e.g. the supporting wire loop. No such event presumably occurs with the droplet placed precisely at the focus; this mechanism evidently cannot take place within the liquid, since using a denser medium to absorb the laser energy involves a much higher heat capacity per unit volume. Dyeing the propellant with methylene blue makes no difference, nor does the use of cardboard (into which the laser normally punches a hole) wetted with propellant lead to any decomposition of the non - military propellant.

In the next sequence of experiments, the propellant droplet was exposed to the plasma and associated shock wave generated by focusing the laser in air, instead of allowing the laser beam to interact with the propellant direct. focusing the Q-switched laser with a short focal length

lens in the air adjacent to the droplet, or close to the wire loop which supports it, shows clear indications of some of the propellant having reacted. The droplet break up is accompanied by the production of a puff of smoke which remains visible for more than 10 seconds. At the same time, a carbon deposit is left on the wire loop. High speed cine shadowgraphy (see Fig. 1) shows the major features of the process: the plasma luminosity around the focal point of the Q-switched beam, the shock wave from the laser generated plasma, which has a very high Mach number initially, and its various reflections, and what appears to be the burning of the propellant spreading over the surface of the droplet from the initial plasma kernel. The last steps in this sequence are absent when a droplet of saline is substituted for the propellant.
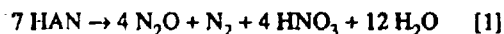
The three sequences shown in Figure 1 illustrate the various parameters investigated. These include the energy of the laser beam and the distance between the position of the laser focus and the droplet. Moreover, double firing the laser can be used to inject a second plasma kernel into the environment of a drop that is already disintegrating. The records make it possible to analyse the interaction with the propellant droplet of a rapidly expanding shock wave, as well as the more slowly developing plasma kernel, and illustrate the wide variation in the rate and completeness of the burning of the droplet that can be achieved. It appears that the shock wave emanating from the laser-generated plasma shatters the droplet surface (the inertia of the droplet is too large for the body of it to be moved, on this time scale) and the fine filaments of liquid propellant which result ignite when they become engulfed by the plasma. This makes the intensity of burning very dependent on the relative positioning of the droplet and laser focus. A second laser pulse (e.g. 200µs, 3rd sequence Fig.1) interacting with the disintegrating and burning fragments from the first provides an additional means of promoting rapid decomposition.
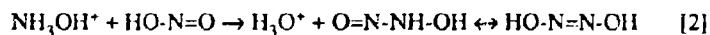
4. Chemical Mechanisms

Speculation regarding the underlying chemistry and relevant reaction steps is particularly interesting in the present context, since this is the first initiation by a plasma which does not

involve the release of products of electrolysis into the propellant (though there is the possibility that NO formed from air in the laser plasma may have some effect).
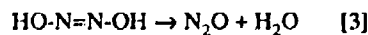
The initiation of reaction involves only the HAN (hydroxyl amonium nitrate) component since identical data are obtained with propellant or with HAN of comparable concentration. Reaction initiation, in contrast to ignition, is essentially independent of pressure, indicating that these early reactions are taking place in the liquid phase. Approximately 80% of the gas obtained is N_2O, 17% is N_2, and the remaining 3% are NO and NO_2. The overall stoichiometry is closely approximated by:

$$7 \text{ HAN} \rightarrow 4 \text{ N}_2\text{O} + \text{N}_2 + 4 \text{ HNO}_3 + 12 \text{ H}_2\text{O} \quad [1]$$

Reaction initiation can be chemically induced by materials such as NO, NO_2, strong acids, and nitronium salts and suggest that the nitronium ion, NO^+_2, is the species that initiates the reaction sequence. Dissociation of HAN into hydroxylamine and nitric acid encourages formation of NO_2. An irreversible reaction, attack by NO^+_2 on NH_2OH, creates nitroxyl, H-N=O, and nitrous acid, HO·N=O, both of which will react with HAN. The reaction of nitrous acid with NH_2OH^+ is nitrosation of hydroxylamine, producing hyponitrous acid, HO-N=N-OH:
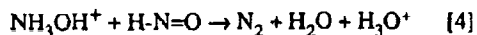
$$NH_3OH^+ + HO\text{-}N\text{=}O \rightarrow H_3O^+ + O\text{=}N\text{-}NH\text{-}OH \leftrightarrow HO\text{-}N\text{=}N\text{-}OH \quad [2]$$

which decomposes rapidly to N_2O:

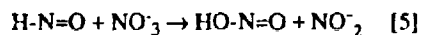$$HO\text{-}N\text{=}N\text{-}OH \rightarrow N_2O + H_2O \quad [3]$$

At the early stages of the reaction sequence, the NH_3OH^+ concentration substantially exceeds the concentration of nitrous acid so that reactions [2] and [3] would essentially remove all of the HO·N=O.

Nitroxyl, H-N=O, the second product of the HAN decomposition, is able to react with HA$^+$, producing N_2:

$$NH_3OH^+ + H\text{-}N\text{=}O \rightarrow N_2 + H_2O + H_3O^+ \quad [4]$$

but reactions [3] and [4] would result in equimolar yields of N_2O and N_2, in contrast to the yields observed in which the N_2O / N_2 product ratio is approximately 4. Reduction of nitrate by nitroxyl, especially in the presence of acid, is more strongly favoured than reaction [4]:

$$H\text{-}N\text{=}O + NO_3^- \rightarrow HO\text{-}N\text{=}O + NO_2^- \quad [5]$$

and 2 moles of HO-N=O would be produced by reaction [5] for each mole of H-N=O removed. The overall stoichiometry established by the proposed reaction scheme is very close to the experimentally observed product yields.

Both NO and NO_2 appear as products in the later stages of the reaction sequence. Nitrous acid is thermally unstable, decomposing to NO, NO_2, and water and may be the source of these gaseous products. The fact that TEAN (triethanol amonium nitrate) is recovered essentially unreacted may also attest to the nonavailability of HO-N=O for reaction late in the HAN decomposition. The described HAN decomposition is exothermic and, as reactions progress, the mixture is sufficiently heated to where both water and nitric acid appear as gases to a significant extent. HNO_3 in the gas phase does not act as an acid but instead undergoes free-radical dissociation, producing the powerful oxidising species, OH and NO_2, both of which can react with any species capable of oxidation.

Experimental data obtained under circumstances where full ignition is achieved, requires confinement or pressurisation. The pressurisation requirement indicates that reaction now takes place either in the gas phase completely or involves two-phase gas-liquid reactions. The reactions are sequential and adequate time must be made available for the initiation reactions to

proceed if ignition is to be observed. The presence of NO or NO_2 in the gas phase facilitates ignition and, indeed, reaction can be observed without thermal input or pressurisation if sufficient NO or NO_2 is available. This is relevant to previously observed micro-explosions on emergence of the jets from plasma plugs.

Although little of the TEAN in propellant is consumed during reaction initiation, its oxidation to CO_2, N_2, and H_2O during combustion releases the majority of the energy contained in the propellant. TEAN, the nitrate salt of triethanolamine, is in equilibrium with the base and nitric acid. As reaction progresses and the temperature is raised, TEAN droplets are formed, and the probability of dissociation increases. The nitric acid released would readily oxidise the amine. Aliphatic amines in general are sensitive to oxidation even under ambient conditions and the elevated temperatures and close proximity of a strong oxidising agent would encourage such reactions. TEAN is too fuel-rich to be oxidised to any large extent by its nitrate ion and the reactive products of the HAN decomposition are needed to achieve complete oxidation. In addition to being the salt of a tertiary amine, TEAN, in contrast to the fuel components of the non - military mixtures, is also a primary alcohol and, as such, reacts with nitrous and nitric acid to produce either nitrite or nitrate esters. All of the reactions previously mentioned that consume HO-N=O limit nitrite ester formation. The nitrate esters are produced by the nitronium ion, NO^+_2, the same species that initiates reaction with HA^+. For nitrate ester formation to be consequential, the rate of nitration would have to be higher than the HA^+ reaction rate, although the existence of three OH groups per TEA^+ would require that the rate of nitration be only 2.3 times faster than the HA^+ reaction rate for equimolar consumption of nitronium. The nitrate esters formed from TEAN would be expected to remain in solution during the early stages of propellant reaction and, quite possibly, the slow reactions observed in TEAN droplets are due to the formation and slow decomposition of small amounts of such esters.

Another possible reaction of TEAN is its combination with NO_2, which results in the production of nitro compounds. Because the production of NO_2 normally is observed only at the later stages of reaction, formation of nitro compounds in the propellant mixture would be unlikely although the slowly reacting TEAN droplets may be evidence of TEAN reacting with NO_2 since the NO_2 content of the venting plumes is quite high.

The initiation phase of reaction produces a spray of molten TEAN droplets in a cloud of hot N_2O, NO, NO_2, and $HO-NO_2$, the various oxidising gases. If temperature is sufficiently high then conditions should be rife for ignition of the mixture. The density of the molten TEAN exceeds 1.2 g/ml and a droplet would require 30 times its volume of NO_2 at 1000°C and 136 atmospheres for complete combustion thus emphasising the strong dependence on pressure of the combustion process. The majority of the energy stored chemically in the propellant is released by the oxidation of TEAN and heat evolution should increase rapidly as ignition progresses.

It is this background which made it particularly desirable to investigate any effect of precursory electrolysis, and the solution of its products in the propellant, on laser initiation.
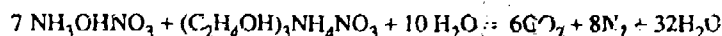
5. Dilatometry

Optical records give only a qualitative indication of the various events which occur during laser initiation. In particular, they do not allow any assessment of the proportion of propellant decomposed. To this end a special dilatometer device - see Fig. 2 - has been designed and constructed to measure the volume of gas released, based on the same general concept as the "calorimeter" described in Ref 2.

The device was constructed of a Perspex cylinder, 25 mm in diameter and 50 mm long. The truncated conical cavity of approx. 4.4 ml, was constructed to minimise volume and to accommodate all the incident laser light. The interchangeable glass disc of 0.6 mm thickness is

held against a gasket by the pressure of the collar and lens, as shown. The position of the laser focus is thus fixed. This was arranged to be adjacent to the droplet, so that comparisons could be made across the entire range of propellant compositions, since focusing into the droplet would initiate reaction only in the military propellant. The assembly of platinum wire electrodes terminating in a loop surrounding a central wire is precisely located by means of a screw thread, which also makes it removable for propellant recharging. A hypodermic syringe is used to deliver and meter each new droplet. The entire dilatometer is attached to the arm of a three-axis positioner using a locating notch and a metal band fastening. The cavity is connected to a small volume capillary tube with a horizontal section along which a mercury droplet is free to move. A small cotton wool plug is inserted in the pipe, ahead of the mercury droplet, in order to damp any pressure surges or shock waves that might otherwise shatter or eject the mercury droplet out of the tube.

The explosive gas and heat evolution following laser initiation of the propellant droplet causes the mercury index to move to its furthest point. Thereafter the confined gas cools, causing the mercury to retract, until it eventually reaches an equilibrium position from which the permanent volume of gas generated can be deduced. In principle, therefore, two measurements are possible: the gas (cold) generated during the decomposition and the initial throw due to its being heated. Since, however, the energy release is linked to the amount of propellant decomposed, it is generally possible to concentrate on the former measurement which is the easier and more accurate. The complete HAN/TEAN decomposition reaction:

$$7 \, NH_3OHNO_3 + (C_2H_4OH)_3NH_4NO_3 + 10 \, H_2O = 6CO_2 + 8N_2 + 32H_2O$$

was used, indicating 1 μmol of propellant to generate 493 μl gas (after condensation of water vapour). The equivalent decomposition for HAN is given by equation [1].

Results are shown in Fig. 3. giving gas volumes, after cooling, generated by (reading from bottom to top) laser discharges in air, near a propellant droplet, and the same after specified periods of electrolysis. The permanent gas volumes generated by electrolysis alone are also

indicated. Results for HAN/SBAN (secondary butyl amonium nitrate) mixtures proved so similar that a further diagram seemed superfluous.

Several interesting points emerge. The proportion of propellant decomposed in the absence of precursory electrolysis is quite small, notwithstanding the spectacular events seen in Fig. 1. Electrolysis on its own produces little heating and a volume of gas increasing with the duration of the passage of current - as would be expected. Electrolysis followed by laser initiation produces a remarkable increase in decomposition as compared with laser initiation on its own. The additional "throw" also continues to increase with time of electrolysis. With the present apparatus, we have not been able to reach equilibrium due to solution of electrolytic gases in the propellant before reaching decompositions of such violence that the mercury index could not be retained within the capillary.

6. Conclusions

The results of these experiments impact both on the underlying fundamental concepts and on their practical applications. As regards the former, they support the proposed chemical mechanism particularly as regards the prediction of the promoting effect of the early reaction steps, and they help to explain the electrical initiation results obtained in earlier work. As regards the practical aspects of propellants ignition by lasers, two important suggestions emerge: firstly for the provision of an air - propellant interface for the laser to produce breakdown in gas in the case of propellants which cannot be initiated by focusing the laser into the the droplet, and secondly for the means of producing some precursory electrolysis, which greatly enhances the initiation process. A small battery (such as the 6 volts used in the present work) seems quite adequate, and the concept of pre - activating stable propellant formulations immediately before initiation may well be relevant to other forms of propellant ignition also.

7. References

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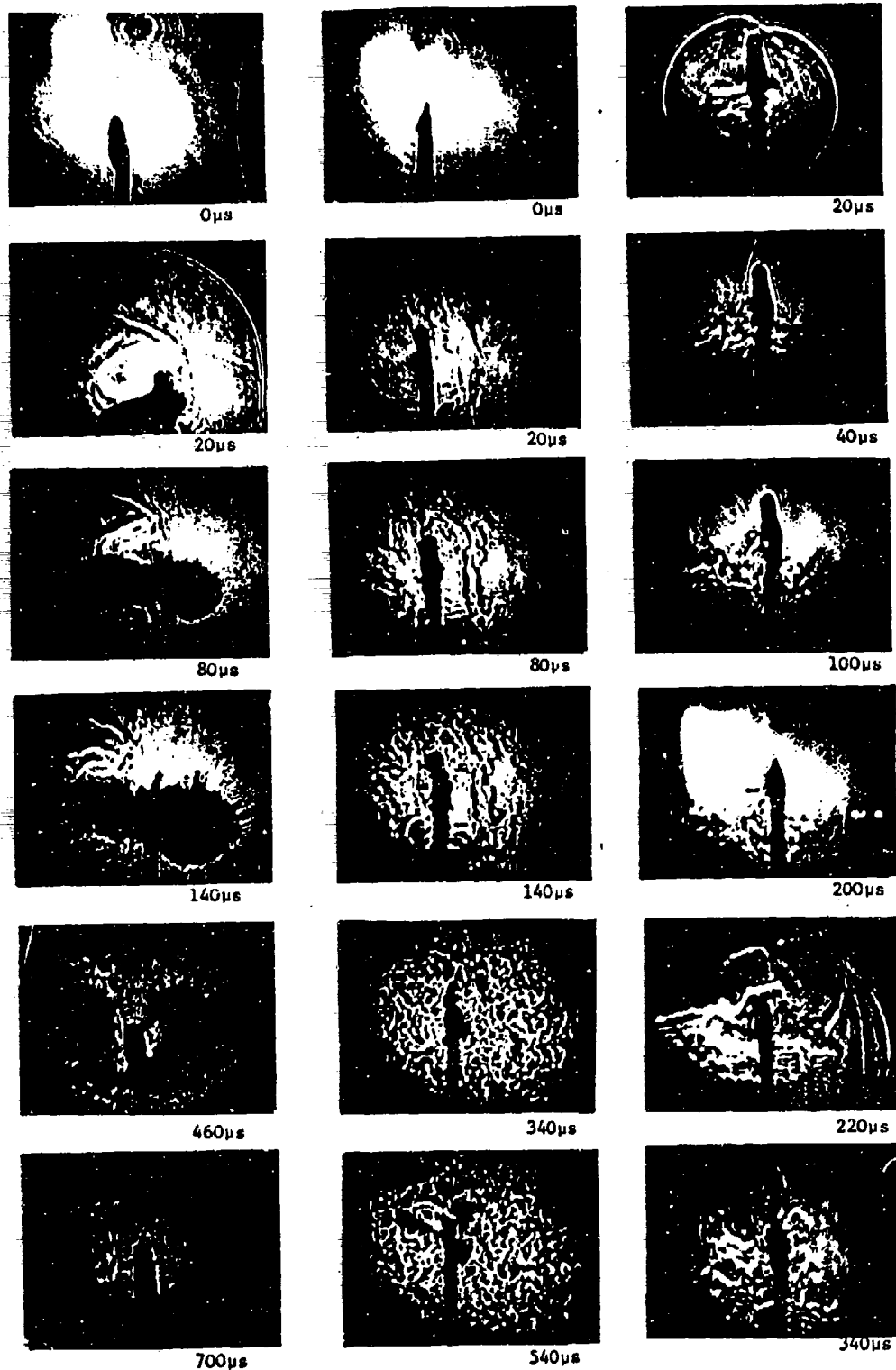
APPENDIX DIAGRAMS

FIG. 1   Three shadow cine sequences illustrating various interactions
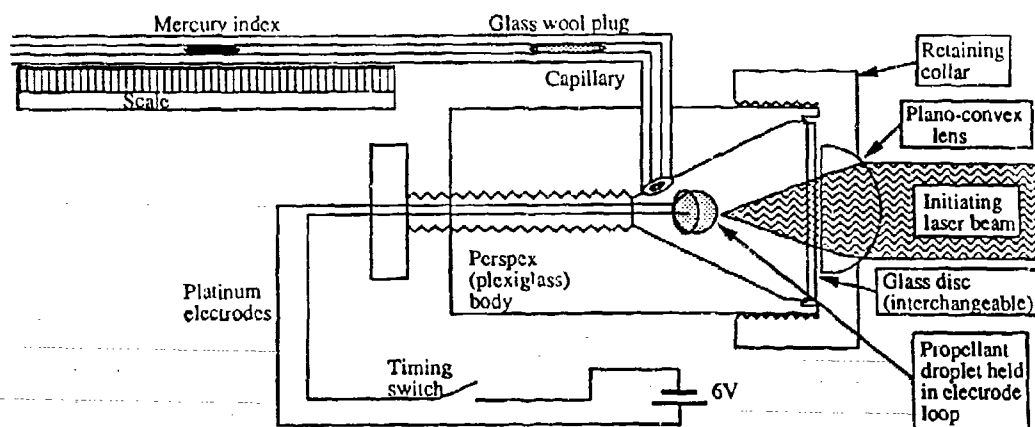between stationary propellant droplet and laser discharge

Mercury index Glass wool plug

Capillary

Scale

Retaining collar

Plano-convex lens

Initiating laser beam

Glass disc (interchangeable)

Platinum electrodes

Perspex (plexiglass) body

Propellant droplet held in electrode loop

Timing switch

6V

Fig. 2. Schematic of dilatometer

Electrolysis for 15 s   Laser discharge

Electrolysis for 10 s   Laser discharge

Laser discharge

Electrolysis for 5s

Laser discharge

Droplets

Laser discharge

Laser discharge

Air alone

BASE LINE

Volume/ µl

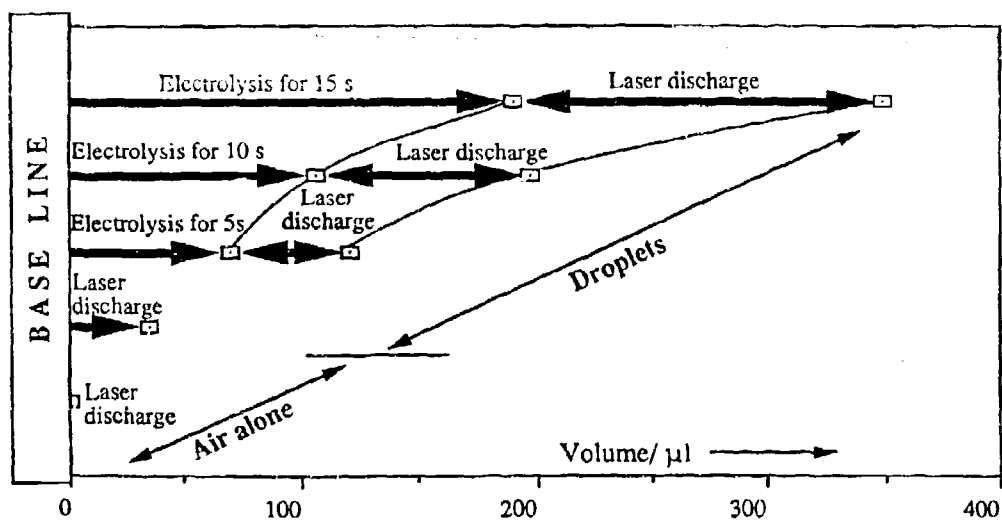0   100   200   300   400

Fig. 3. Permanent (cold) gas volume following laser discharge, electrolysis, or both.